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HAZARD EVALUATION DIVISION
STANDARD EVALUATION PROCEDURE
SOIL PHOTOLYSIS STUDY

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STANDARD EVALUATION PROCEDURE

PREAMBLE

This Standard Evaluation Procedure (SEP) is one of a set of guidance documents which explain the procedures used to evaluate environmental and human health effects data submitted to the Office of Pesticide Programs. The SEPs are designed to ensure comprehensive and consistent treatment of major scientific topics in these reviews and to provide interpretive policy guidance where appropriate. The Standard Evaluation Procedures will be used in conjunction with the appropriate Pesticide Assessment Guidelines and other Agency Guidelines. While the documents were developed to explain specifically the principles of scientific evaluation within the Office of Pesticide Programs, they may also be used by other offices in the Agency in the evaluation of studies and scientific data. The Standard Evaluation Procedures will also serve as valuable internal reference documents and will inform the public and regulated community of important considerations in the evaluation of test data for determining chemical hazards. I believe the SEPs will improve both the quality of science within EPA and, in conjunction with the Pesticide Assessment Guidelines, will lead to more effective use of both public and private resources.


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SOIL PHOTOLYSIS STUDIES

I. INTRODUCTION

A. Objective

This Standard Evaluation Procedure (SEP) is to be used as an aid for Exposure Assessment Branch data reviewers in their evaluations of soil photolysis studies submitted by registrants in support of pesticide registration.

Title 40 Part 158.130¹ requires studies on photodegradation on soil to be conducted with each pesticide active ingredient used on terrestrial food crops, in orchard crops, and in forests. The data can be waived when the active ingredient is injected into the soil or entirely incorporated into the soil during application. This study is also required for a manufacturing-use product which may be used to formulate an end-use product for such uses.

B. General Theory

A general discussion of photochemical principles and of light sources appears in Appendix A (attached). Studies of the photolysis of pesticides on soil surfaces are needed in addition to those conducted in water since the pathways and ultimate products of pesticide degradation may differ significantly from those which occur in water. For example, a photoproduct formed on soil could react with the soil organic matter or be metabolized by soil microorganisms², thus producing possibly unique degradation products.

II. THE SUBMITTED STUDY

A. Purpose

The purpose of these studies is to provide data on pesticide degradation rates and on the formation and decline of photoproducts on soil surfaces. Such data are required to support the registration of pesticides since pesticides are either: (1) intentionally applied to the soil surface, (2) remain on the soil surface due to incomplete soil incorporation³ or, (3) reach the soil surface via drift^{4,5} and/or runoff^{6,7} from treated areas.

B. Study Design

The Subdivision N Guidelines² and the Data Submission Format Guidelines for Photolysis Studies⁸ contain detailed information about what information must be supplied with the soil photolysis

study and under what conditions the study should be conducted. The registrant's report should contain the stated goal and sufficient information on the test protocol (compound purity and type of compound used; detailed description of light conditions; description of soil characteristics; sufficient description of sampling frequency) and the analytical protocol (description of methods used for quantitative, qualitative analyses and reports on the quality control procedures used to ensure the validity of the study).

Specific information that the registrant should include with the study is listed in Appendix B.

III. THE EVALUATION PROCESS

A. Determine the Need for the Study

For all data submitted as part of a registration action, the reviewer is to first determine whether the data is needed in support of the proposed use. The reviewer should also examine the proposed use pattern to determine if there are conditions that would support the selection of special test parameters (e.g., soil texture or organic matter content, incident light wavelength or intensity, or photoperiod) that would more closely approximate field conditions. If an initial look at the study reveals that the data supplied is not relevant and not needed to support the proposed registration action, then the reviewer should only mention in the review that the particular study was submitted but was not reviewed and why.

B. Read the Report

Read the soil photolysis report keeping the following broad issues in mind: (1) Are the goals appropriate; (2) Was the study conducted in a scientifically sound manner to meet those goals; (3) Was the experimental design, test substance and experimental procedures adequately described; and, (4) Are there data gaps that impede the review process or invalidate the study?

C. Prepare the Data Evaluation

The reviewer should now prepare the Data Evaluation Record (DER) according to the Standard Format for Preparation of Environmental Fate Reviews. Appendices B-D should be used in this process.

1. Write the Technical Evaluation

In the DER of the study, the reviewer is to record (1) whether the submitted study reliably defines the rate of soil photolysis of the a.i., and (2) the identity of the photoproducts present at > 10%. The identity of photoproducts present at < 10%

APPENDIX A

GENERAL THEORY AND REFERENCES FOR EVALUATION OF
SOIL PHOTOLYSIS STUDIES

Photolysis is the interaction of a compound with light in which bonds are broken as a result of the transfer of energy to those bonds.⁹ While photolysis is viewed as a degradation process, compounds are not necessarily broken down into constituent parts or simpler compounds. Sunlight can transform the original compound into compounds of similar or even greater structural complexity.¹⁰

The energy transfer can occur in two ways: (1) directly from the light to the affected compound or (2) indirectly from the light to another compound which then transfers the light energy to the affected compound. The latter process is called sensitized energy transfer.¹¹

The basic law of photochemistry states that only light which is absorbed can effect chemical change in a system.¹² The relationship of wavelength to the energy of one photon of radiation is derived from the following equations:

$$E = hv ; \quad v = c/\lambda ; \quad \text{therefore, } E = hc/\lambda$$

where E is the energy in ergs, v is the frequency in sec⁻¹, h is Planck's constant (6.6 x 10⁻²⁷ erg sec), c is the velocity of the radiation in cm sec⁻¹ and λ is the wavelength in centimeters. Thus, the energy at any frequency can be calculated. Using this equation and comparing typical bond dissociation energies with energy levels associated with molecular transitions in different absorption regions, one finds that only electronic transitions from the UV/visible absorption region are energetic enough to lead to chemical reactions.¹³ Since "the stratospheric ozone layer effectively prevents UV irradiation of less than 290 nm from reaching the ecosphere",¹³ the absorption region of interest is narrowed to 290-750 nm.¹³

19. Quality assurance. A complete description of the measures taken to insure the integrity of the study. This section should include: logbooks and/or record-keeping procedures; representative instrument printouts (chromatograms, spectra, etc.); sample coding; use of replicate samples and control blanks; use of written and validated analytical methodology, including modification(s) made; skilled laboratory personnel; well-equipped laboratory facility; use of high quality glassware, solvents, and test compounds; minimal contamination; calibration and maintenance of instruments; good laboratory practices in handling the test substance(s).
20. Contact for questions from the reviewer.
21. Raw data, sample chromatograms and sample calculations on how the photolysis rates were derived and how the photolysis products were identified.
22. Special problems with the study such as bound residues, etc.

APPENDIX C

CONSIDERATIONS IN REVIEWING SOIL PHOTOLYSIS STUDIES

1. Were the name and structure of the parent and photoproduct(s) provided?
2. Was the starting concentration high enough to permit the isolation and identification of photoproducts formed?
3. Were precautions taken to minimize losses through volatilization?
4. Were appropriate traps utilized to contain volatile products for analysis?
5. Was the radiolabel in a stable portion of the compound?
6. Were sufficient samples taken and at appropriate times during the study? Were adequate replicates made?
7. Did the study continue through at least 1 half-life or 30 days, whichever came first?
8. Was the pesticide applied to the soil in a uniform manner?
9. Were there controls, prepared and maintained as for the other samples except that they were kept in the dark?
10. For sunlight as the source, were the following given:
 - a record of the intensity of incident sunlight?
 - time of exposure?
 - latitude?
 - time of year?
 - atmospheric cover?
 - other major variables which affect incident light?
11. For artificial light as the source, were the following given:
 - description of the source?
 - intensity?
 - wavelength distribution? (emission spectrum)
 - time of exposure?
 - the relationship of the light intensity employed to that of natural sunlight?
12. Were filters used in the experimental apparatus to remove wavelengths below 290 nm?
13. Were photoproducts produced in > 10% yield identified?

14. Was there a good material balance?
15. Was a half-life estimate made for the parent compound?
16. Was there an impurity in the a.i. that would interfere with the analytical method?
17. Was the analytical method adequately described? Were statistics verifiable?
18. Were raw data and samples of analytical data sheets, chromatograms, calculations, etc. given?
19. Were control samples, prepared and handled the same as the pesticide treated study samples, run in each experiment?

APPENDIX D

TEST PARAMETERS INFLUENCING SOIL PHOTOLYSIS

1. Experimental Design

From the considerations of Appendix C, the reviewer must draw some conclusions about the influence of the experimental design on the validity of the study for the proposed use. Some questions the reviewer should answer are:

1. Was sunlight, if used, representative of the area of proposed use?
2. Did the emission wavelength spectrum of the artificial source, if used, simulate that of natural sunlight?
3. Was the pattern of light and dark given and was it reasonable for the proposed use pattern? (i.e., 12 hours of light/12 hours of dark per day; 16 hours of light/8 hours of dark per day; etc.)
4. Was the relationship of the intensity of the artificial sunlight used appropriate to that of natural sunlight in the area and for the time of the planned use?
5. Was a suitable method used for measuring the intensity of incident light?

Typical experimental procedures involve mixing the test substance with the soil and forming a thin film on a glass plate from a slurry (see for example ref. 14) or spraying the test substance on a pre-formed thin soil layer. To reduce error, a single, pesticide-fortified slurry should be used to coat the glass plates or, the untreated, pre-formed soil thin layers should be brought next to each other and be sprayed at the same time.

The amount of the test substance initially applied will depend on the analytical method, the proposed application rate, plus other factors. The initial concentration must clearly allow the isolation and identification of photoproducts formed and have representative results indicative of what would occur under use conditions. Samples periodically taken from the irradiated films are then analyzed for both the parent compound and any degradation products. Similar thin films held under identical conditions but kept in the dark serve as controls to demonstrate that any observed reactions are in fact photochemically driven.

2. Nature of Light and Factors Effecting the Incident Light

The light source used for sample irradiation may be either natural or simulated sunlight. If natural sunlight is used, a record of its intensity and wavelength distribution is required as well as the time of exposure, latitude, time of year, atmospheric cover, and other major variables which affect incident light. If an artificial light source is used, its intensity, wavelength distribution and the length of exposure are required as well as the relationship of the light intensity employed to that of natural sunlight. Samples should not be exposed to radiation below 290 nm, the cut off point of the solar spectrum at the earth's surface. If an artificial light source emits radiation below this level, suitable filters should be used.

The reviewer should be aware of seasonal differences in natural sunlight when evaluating photolysis data. The half-life of a pesticide can vary by a factor of three during exposure to spring versus summer natural sunlight¹⁵. Also, the results of a photolysis experiment under natural sunlight should not be extrapolated from one location to another because the intensity of solar ultraviolet radiation at the earth's surface is a function of latitude, season and elevation¹⁶. This is particularly true for the 300-320 nm region¹⁶ which is a subset of the 290-450 nm region in which most photolysis reactions probably occur¹⁷.

Various kinds of glass absorb and transmit different wavelengths.¹³ Therefore, the kind of glass (both in vessels and filters) should be specified and its transmissibility considered in evaluating the adequacy of the study. Also, the reference which gives the transmissibility of the glass should be current, as the glass manufacturing processes have changed with a concomitant change in transmissibility of glass batches.¹⁸ Quartz is the glass of choice with borosilicate glass as an acceptable choice.¹⁹ The reviewer should be aware that borosilicate glass varies with manufacturer.¹⁹

3. Radiolabeling

Use of radiolabeled pesticides as test materials provides easier and more reliable accountability of material balance than use of non-labeled material. Radiolabeling should be done in a stable portion of the molecule. Generally, tritium labeling is less reliable because of proton exchange with the medium. If the parent compound forms two or more significant photoproducts, it may be necessary to label the parent compound at more than one site in the molecule so that the degradation pathway may be more completely and easily followed. For a complete discussion of the use of radiolabeling in environmental fate studies submitted to EPA, see the SEP for Hydrolysis Studies²⁰.

4. Mass balance considerations

All of the radioactivity used in the experiment must be accounted for to ensure that all the photoproducts have been detected and that the fate of all the starting material is traced. In particular, the study must demonstrate that no radioactivity is lost through volatilization. Therefore, traps must be used to monitor production of volatile photolysis products, such as carbon dioxide and humidified air should be drawn through the system. In addition, the temperature of the soil should be monitored and maintained at 20° to 30°C (as should the dark controls).

5. Soil selection

The soil chosen should initially be pesticide free to eliminate interference during analysis. The soil chosen should also be taken from the surface of the field since sunlight does not penetrate soil; therefore, photolysis occurs at the surface. Also, soil at the surface is most rich in organic matter²¹ of which a component, humic acid, has been shown to be a photosensitizer²². Using subsoil, therefore, in a photolysis study would not give results representative of photolysis at the surface.

The test soil used should be the same as one of those used in the aerobic soil metabolism study, so that direct comparisons can be made between microbial and photochemical pathways of degradation. If necessary, a variety of soils should be used which represent the likely range of soil types to be encountered under actual use.

6. Duration, Sampling and Identification of Photolysis Products

Sufficient data points should be taken to allow the estimation of the half-life for disappearance of the parent compound. In general, an irradiation regime equivalent to a thirty-day duration of the experiment (° 12-hour light:12-hour dark) is adequate. However, where photodegradation is a significant degradation pathway or where photoproducts of particular environmental or toxicological interest are formed, a longer duration of the experiment may be necessary to establish rates of reaction or structures of products. Taking four samples for analysis, with one sample taken at the half-life or at the conclusion of the 30-day test period has been recommended.² However, it is recognized that other sampling regimens (i.e., involving more frequent and additional sampling) may be necessary in some cases.

At each sampling interval, data to prepare a mass balance should be obtained. This requires simultaneous sampling and analysis of the soil and volatiles traps.

Degradation products produced in greater than about ten percent yield should be chemically identified. The structures of the photoproducts should be given and an overall degradation pathway provided. In some cases, it may be necessary to synthesize a particular photolysis product for further degradation studies. As a practical matter, if less than about 10% of the pesticide photodegrades within a thirty-day study period, the pesticide is usually considered photolytically stable in soil.

7. Analytical Method

A detailed description of the analyses used to determine the parent and photoproducts should be given. The following information should be included:

1. Name (and signature), title, organization, address, and telephone number of the person(s) responsible for the planning/supervision/monitoring and laboratory procedures/analyses.
2. Analytical method(s) title/designation/date.
3. Source of analytical method(s) [e.g., Pesticide Analytical Manual (PAM), Vol. II, scientific literature, Company reports, other].
4. Principles of the analytical procedure [describe].
5. Non-Confidential Business Information (non-CBI) copy of the analytical method(s) detailing in stepwise fashion the procedures (extraction, clean-up, derivatization, determination, calculation of the magnitude of the compound(s)).
6. Reagents or procedural steps requiring special precautions [to avoid safety and health hazards, explain].
7. Identification of the chemical species determined.
8. Modifications, if any to the analytical method(s) [detail].
9. Extraction efficiency [if pertinent].
10. Instrumentation [make/model; type/specificity of detector(s) column(s) (packing materials, size); carrier gas(es); flow rate(s); temperature(s); voltage; limit of detection and sensitivity; calibration procedures; etc.].
11. Interference(s), if any [describe].
12. Confirmatory techniques [e.g., different column packing(s) or detector(s), etc.].

13. Sample identification [coding and labeling information; should be the same as - or cross-referenced to - the sample coding/labeling assigned at harvest].

14. Results [raw data; laboratory worksheets; stepwise calculation of levels; dilution factors; peak heights/areas; method correction factor(s) applied (e.g., storage stability and method validation recovery values); formula(e)/standard curve(s) used; amount found of total applied, and of individual component(s) (i.e., photoproducts); range of values; representative chromatograms; spectra, etc. (as applicable) from control and treated samples; etc.]

15. Statistical treatment(s) [describe test(s) applied to the raw data].

16. Quality assurance [control measures/precautions followed to ensure the fidelity of determinations, including logbooks and record-keeping procedures; representative instrument print-outs (chromatograms, spectra, etc.); sample coding; use of replicate samples and control blanks; use of written and validated analytical methodology for analyses, including modification(s) made; skilled laborator personnel; well-equipped laboratory facility; use of high-quality glassware, solvents, and test compound(s); minimize contamination; calibration and maintenance of instrumentation; good laboratory practices.

17. Time required for analysis [to carry a sample completely through the analytical procedure, including the determinative step].

18. Other [any and all additional information the petitioner considers appropriate and relevant to provide a complete and thorough description of residue analytical methodology and the means of calculating the residue results].

8. Additional Considerations

Factors that affect the rate and products of photolysis on soils are not well understood at present.¹⁹ Dr. Richard Zepp, research chemist, EPA-RTP, has suggested that based on limited studies the following factors appear to be very important and should be considered in this SEP. They are only raised now as points which need to be addressed.

1. Soils contain organic (humic) and mineral substances that strongly attenuate sunlight and that can photosensitize and/or quench light-induced transformations.²³ The net effect of the various photochemical influences of these soil components is difficult to predict quantitatively, because little research has been done in this area. It seems clear, however, that the light attenuation effect reduced the penetration of sunlight to no more

than about 1 mm. Variability in the extent of light attenuation is likely to be a major reason for lack of precision in the determination of pesticide photolysis rates.

2. Recent studies by Gohre and Miller²⁴ have shown that sunlight absorption by soils leads to production of singlet oxygen, a reactive, excited form of dioxygen. Singlet oxygen reacts rapidly with certain pesticides and also is known to react with natural substances to form other reactive oxidants such as peroxides. The likely precursors of singlet oxygen, soil components in their excited triplet states, are likely to be chemically reactive. This finding strongly indicates that sunlight-induced transformations of pesticides that do not even absorb sunlight may be significant on soil surfaces. This is consistent with earlier findings in field studies that certain cyclodiene insecticides such as aldrin are transformed on soils even though they are transparent to ground-level solar radiation. These indirect photoreactions could vary dramatically in rate constant and products from one soil to another.

3. As mentioned in section 1 of these comments, all of the solar radiation is absorbed in the top millimeter, and a substantial portion is transformed into thermal energy. Soil surfaces get very hot under sunlight and the heating may accelerate various nonphotochemical reactions of pesticides, e.g., hydrolysis, oxidation. Thus, if the soil is not cooled as in Hautala's²⁵ studies, thermal reactions are likely to make a significant contribution to pesticide loss in the soil, especially with hydrolyzable pesticides such as esters, ureas, carbamates, and phosphorothioates. It seems clear that soil temperature and its effects in thermal reactions are extremely important considerations in evaluating soil photolysis data.

4. Hautala's²⁵ studies showed that the moisture content of soils has an important effect on photolysis rates of certain pesticides and that the nature of the effect is altered in the presence of surfactants, substances that are often co-applied with active ingredients of pesticide formulations. These results also indicate that the mode of application of the pesticide to the soil may have important effects on photolysis rates, and that the photoreactions are described by first-order rate expressions.

5. Finally, the rate of loss may be influenced by physical processes such as sorption/desorption. Recent studies²⁶ with the hydrophobic, chlorinated-pesticide derivative, DDE, indicate that the photochemical behavior of a pesticide depends on the amount of time between application and the start of the irradiation.

Based on these comments, it has been suggested¹⁹ that the reviewer place the heaviest weight on soil photolysis data obtained using soil from the actual location(s) where the pesticide will

be used. Also, the most meaningful data will be obtained when the pesticide is applied in the same way as in the field prior to photolysis.

REFERENCES

1. Title 40. Protection of the Environment. Chapter 1. Environmental Protection Agency, Subchapter E, Pesticide Programs, OPP 300 63 A. Part 158, Data Requirements for Pesticide Registration. Final Rule. (1984).
2. Pesticide Assessment Guidelines, Subdivision N. Chemistry Environmental Fate. EPA-540/9-82-021. October 1982.
3. Erbach, D.C. and J.J. Tollefson, 1983. Granular Insecticide Application for Corn Rootworm Control. Transactions of the Am. Soc. of Agric. Engineers, pp. 696-699.
4. Yates, W.E. and N.B. Akesson, 1973. Reducing Pesticide Chemical Drift in "Pesticide Formulations", W. van Valkenburg, Ed.; Marcel-Dekker, New York. Chapter 7.
5. von Rumker, M.; G.L. Kelso; F. Horay; K.A. Lawrence. 1975. A Study of the Efficiency of the Use of Pesticides in Agriculture. Contract No. 68-01-2608.
6. Control of Water Pollution from Cropland, vol. 1. 1975. B.A. Stewart; USDA/EPA.
7. Baker, J.L. Agricultural Areas as Nonpoint Sources of Pollution, in "Environmental Impact of Nonpoint Source Pollution", M.R. Overcash and J.M. Davidson, Eds. Ann Arbor Science, 1980. pp. 275-310.
8. Data Submission Format Guidelines for Photolysis Studies.
9. Faust, S.D. and Hunter, J.V., eds. "Organic Compounds in Aquatic Environments," Marcel Dekker, Inc., New York. 1971.
10. Rabek, J.F. "Experimental Methods in Photochemistry and Photophysics, Part 2," John Wiley & Sons, New York, 1982.
11. Mill, T. et. al. "Design and Validation of Screening and Detailed Methods for Environmental Processes," July 1982. EPA Contract 68-01-6325; pp. 35-86.
12. Wolfe, N. Lee et. al. "Chemical and Photochemical Transformations of Selected Pesticides in Aquatic Systems," September 1976. EPA-600/3-76-067; pp. 12-28.
13. Turro, Nicholas "Molecular Photochemistry," W.A. Benjamin, Inc., New York, 1967.
14. Smith, C.A., Y. Iwata, and F.A. Guthrie, 1978. Conversion and Disappearance of Methidathion on Thin Layers of Dry Soil. J. Agr. Food Chem. 26(4): 959-962.

15. Koshy, K.T., A.R. Friedman, A.L. van der Slik, and D.R. Graber. 1975. Photolysis of Benzoic Acid 2-(2,4,6-trichlorophenyl) hydrazide. J. Agr. Food Chem. 23: 1084-1088.
16. Bener, P. Approximate Values of Intensity of Natural Ultraviolet for Different Amounts of Atmospheric Ozone. Davos Platz, Switzerland. Report # DAJA37-68-C-1017. U.S. Department of the Army. June 1972.
17. Crosby, D.G. Herbicide Photodecomposition; In: Herbicides: Chemistry, Degradation, and Mode of Action, Ed. Kearney, P.C. and Kaufman, D.D., vol. 2, Marcel Dekker, Inc., 1976.
18. Personal Communication, Stuart Cohen, EPA.
19. Personal Communication, Richard Zepp, EPA.
20. SEP for Hydrolysis Studies.
21. Brady, N.C. The Nature and Properties of Soils, 8th ed., Macmillan Publishing Co., Inc., New York, 1974.
22. Zepp, R.G.; G.L. Baughman; P.F. Schlotzhauer. Chemosphere 1981. 10, pp. 109-117.
23. Miller, G.C. and R.G. Zepp. Extrapolating photolysis rates from the laboratory to the environment. Residue Reviews 1983. 85, pp. 89-110.
24. Gohre, K. and G.C. Miller, J. Agr. Food Chem. 31: 1164-1168.
25. Hautala, R.R. Surfactant Effects on Pesticide Photochemistry in Water and Soil. EPA Final Report EPA-60/3-78-060, 1978.
26. Zepp, R.G. and P.F. Schlotzhauer. Effects of Equilibration Time on Photoreactivity of the Pollutant DDE Sorbed on Natural Sediments. Chemosphere 1981. 10, pp. 453-460.